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ORIGINAL ARTICLE

Correlation between the structure and biological activity studies of supramolecular coordination azodye compounds

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KEYWORDS

(4-Alkylphenylazo)-5-sulfo-8-hydroxyquinolines (HL_n); Cu(II)/Ni(II) complexes; Hydrogen-bonding stability; Spectroscopic studies; Antimicrobial activities

Abstract A series of novel bidentate azodye quinoline ligands were synthesized with various *p*-aromatic amines like *p*-(OCH_3, CH_3, H, Cl and NO_2). Novel azodye (HL_n) and complexes [Cu(II)/Ni(II)] of these ligands have been characterized on the basis of elemental analysis, molar conductance and magnetic measurements, infrared and electronic spectral studies. Suitable structures have been proposed for these complexes. The synthesized ligands and their metal complexes were screened for their antimicrobial activity against four local bacterial species, two Gram positive bacteria (*Bacillus cereus* and *Staphylococcus aureus*) and two Gram negative bacteria (*Escherichia coli* and *Klebsiella pneumoniae*) as well as against four local fungal species; namely *Aspergillus niger*, *Alternaria alternata*, *Penicillium italicum* and *Fusarium oxysporium*. The tested compounds have good antibacterial activity against *B. cereus, E. coli* and *K. pneumonia*e. Very low effect was detected against *S. aureus* and *F. oxysporium*. We found that the results of antifungal activity of HL_n revealed that the complexes are more toxic than ligands against fungi due to the transition metal involved in the coordination. Also Cu^{2+} complexes are more active than Ni^{2+} complexes against *B. cereus*, *E. coli* and *K. pneumoniae*. The size of the clear zone was in the following order *p*-(OCH_3 < CH_3 < H < Cl < NO_2) as expected from Hammett's constants σ^R.

1. Introduction

The coordination chemistry of Cu(II)/Ni(II) is more interesting and rather more important because of two main reasons. The vanadyl complexes have found increasing importance as a model in biological systems (Sakurai et al., 2003, 2004; Smith et al., 2002). The coordination number and geometry of this metal is highly ligand dependent (Holloway and Melnik,

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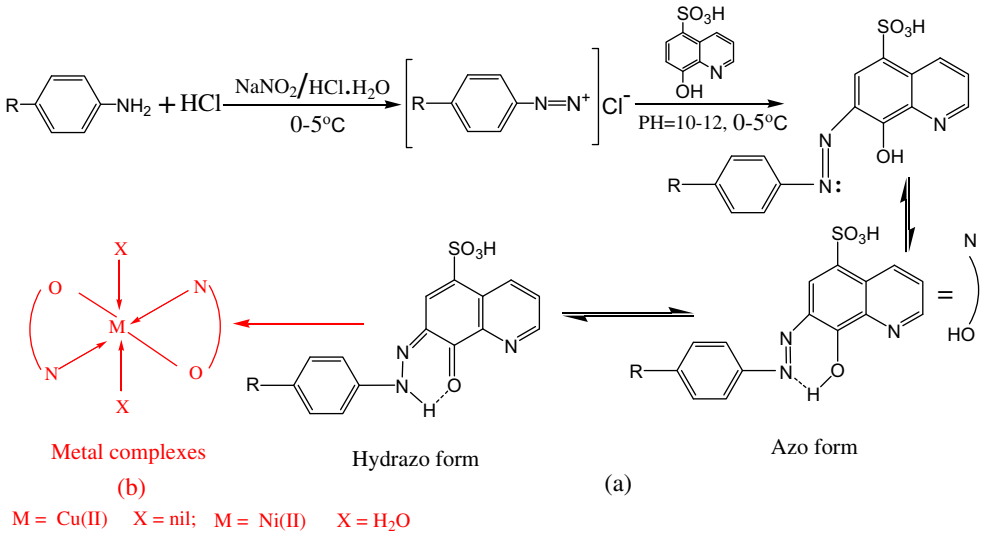

Figure 1 The formation mechanism of azodye ligands (HL_n). $n = 1$, $R = OCH_3$ (HL_1); $n = 2$, CH_3 (HL_2); $n = 3$, H (HL_3); $n = 4$, Cl (HL_4); and $n = 5$, NO_2 (HL_5).

Table 1 Elemental analysis (C, H, S and N)[a], color and yield (%) of the ligands.

Compound[b]	Color	Yield (%)	Exp. (Calcd.) %			
			C	H	N	S
HL_1	Black	60.4	53.88 (53.48)	3.82 (3.62)	12.21 (11.70)	9.35 (8.91)
HL_2	Red	62.0	56.12 (55.98)	3.90 (3.79)	12.72 (12.25)	9.71 (9.33)
HL_3	Pale red	64.7	54.87 (54.71)	3.45 (3.34)	13.22 (12.77)	10.10 (9.73)
HL_4	Red	68.8	49.64 (49.52)	2.84 (2.75)	11.93 (11.55)	9.21 (8.80)
HL_5	Dark red	78.0	48.30 (48.13)	2.72 (2.67)	15.30 (14.97)	8.83 (8.56)

[a] The excellent agreement between calculated and experimental data supports the assignment suggested in the present work.
[b] HL_1–HL_5 are the ligands as given in Fig. 1.

1985) and vanadyl complexes have been reported to be less toxic than vanadate ions (Hudson, 1996). Therefore, the Schiff base complexes of vanadyl ion are topic of many research reports (Maurya and Raiput, 2006; Boghaei et al., 2006). Azo compounds have gained a paramount attention due to their use as models for biological systems (Pati, 1975; Pearce et al., 2001). The driving force for investigating and developing an understanding in the coordinating behavior and chemical equilibrium of these novel compounds is based on the importance of studying the metal–ligand affinities, stereochemistry and substitution properties of the complexes involved (El-Sonbati et al., 2004a, 2012a). Efforts have been made to carry out detailed studies to synthesize and elucidate the structural and electronic properties of novel families of complexes with quinoline derivatives as novel chelating bis-bidentate azodye models.

(4-alkylphenylazo)-5-sulfo-8-hydroxyquinolines (HL_n) and their related compounds (Fig. 2A′) have been extensively used as ligands in the transition metal coordination chemistry (El-Sonbati et al., 2002a,b, 2004b, 2007). Ease of synthesis, favorable steric arrangement and variability of donor sites that these ligands possess with suitable constituents, make this family an excellent candidate for constructing new families of complexes which are of great intriguing interest for the coordination chemistry. Although, no structural chemistry or coordinating and biological studies have been reported on ligands containing both azo and quinoline function groups, data from our laboratory (El-Sonbati et al., 2002a,b, 2004a,b, 2007) have demonstrated that the bis-bidentate azodye ligands play a key role in making new complexes with transition metal ions. However, little is known concerning the constituents of these complexes, as well as the chemistry involved in their preparation, or the structure and coordination in such complexes. It has been shown from the IR spectral data that the hydrogen bonding plays an important role in biological systems (Pearce et al., 2001). Due to the higher number of hydrogen bonds, the Watson–Crick pair of guanine and cytosine is more stable than the thymine–adenine complex (Ebert, 1993). Moreover, Jorgensen and El-Sonbati et al. (Jorgensen and Pranata, 1990; El-Sonbati et al., 2002a, 2004b, 2007, 2010a, 2012b) found out that the stability of multiple hydrogen bonded

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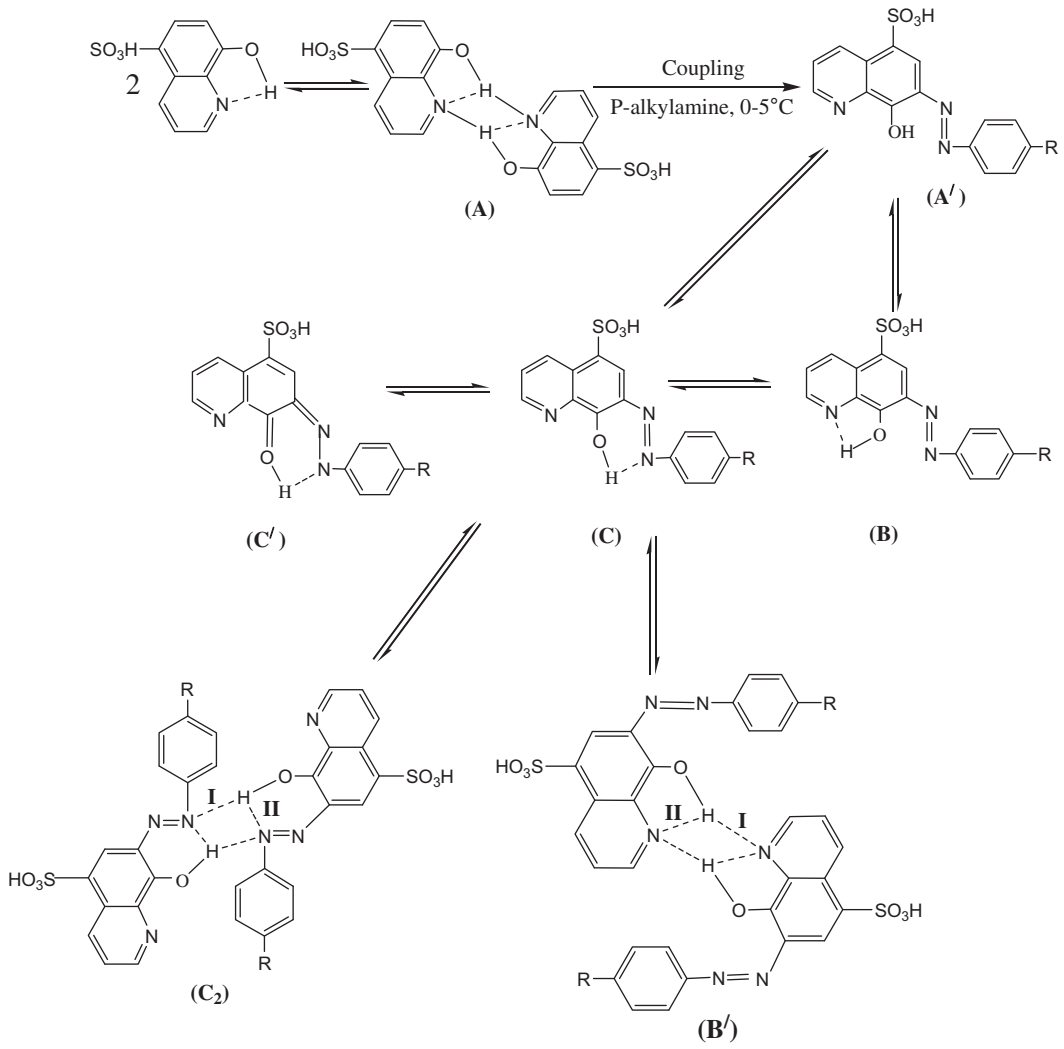

Figure 2 Representation of the dimeric structure and intramolecular hydrogen bond.

"dimers" depends not only on the number of hydrogen bonds but also on the hydrogen bonding pattern. The importance of clarifying the structure and stability of hydrogen-bonded complexes has opened up an area of surface science that has attracted a considerable attention in the environmental chemistry.

8-Hydroxyquinoline is well known as an analytical reagent (Jeffery et al., 1989; Ivanor and Metkina, 1978). Its various derivatives are also useful in pharmaceutical compounds (Bruckhalter et al., 1954). Several azo dyes based on 8-quinolinol (8-HQ) are also reported for dyeing of textiles as well as their chelating properties. Various derivatives based on quinolinol have also been reported for their chelating property. The literature survey reveals that the azo dyes based on sulfanilamide of 8-HQ have not been reported so far.

In this paper, we investigate the supramolecular chemistry of azo 8-hydroxyquinoline derivatives regarding the metal coordination as well as the behavior of hydrogen bonding of these molecules. These are achieved by reporting the studies of (i) the synthesis of novel (4-alkylphenylazo)-5-sulfo-8-hydroxyquinoline (HL_n) ligands, (ii) the synthesis of Cu(II)/Ni(II) complexes derived from these ligands, (iii) investigating the stereochemistry of the complexes based on the electronic spectra and other measurements, (iv) determining the vibrational mode of bonding, stability and structures of the hydrogen-bonding complexes, (v) studying the antimicrobial activity of (HL_n) and their complexes, and (vi) comparing antimicrobial activity results of (HL_n) and their complexes with the standard antibacterial and antifungal drugs.

In addition to the above mentioned aims, we will discuss the previous studies of hydrogen bonding (Albrecht et al., 2000) and compare them with the results of the present paper in order to provide a better explanation and justification to the chemical behavior of such complexes and biologically allowing the reversible formation of aggregates which are non-covalently linked.

2. Experimental

All the chemicals used were of British Drug House (BDH) quality. 5-sulfo-8-Hydroxyquinoline (sulfooxine) was prepared by the method outlined by our group. The experimental technique has been described previously (El-Sonbati et al., 2002a,b, 2004a,b, 2007, 2010a,b).

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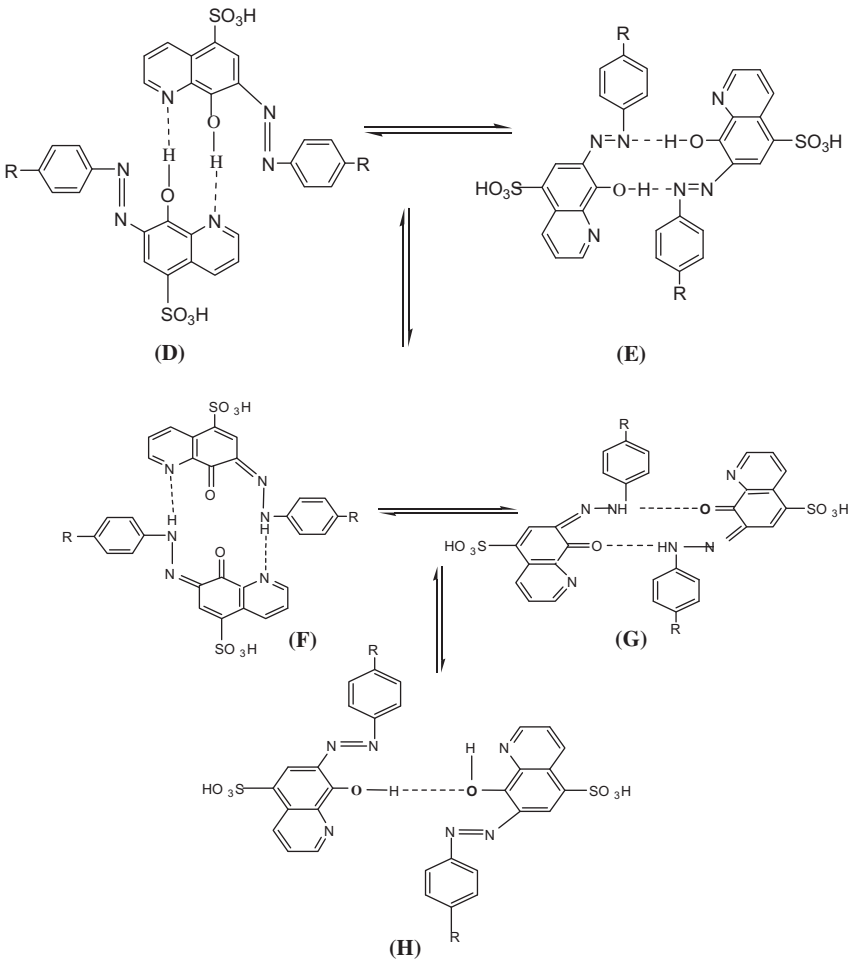

Figure 3 Intermolecular hydrogen bond.

2.1. Synthesis of ligands

(4-Alkylphenylazo)-5-sulfo-8-hydroxyquinolines (HL_n) were typically prepared by adding 25 mL of distilled water containing hydrochloric acid (12 M, 2.68 mL, 32.19 mmol) to aniline (10.73 mmol) or *p*-derivatives. To the resulting mixture, stirred and cooled to 0 °C, a solution of sodium nitrite (10.73 mmol, in 20 mL of water) was added dropwise. The so-formed diazonium chloride was consecutively coupled with an alkaline solution (sulfonate) (10.73 mmol) in 20 mL of ethanol containing 602 mg (10.73 mmol) of potassium hydroxide. Immediately, the formed red precipitate was filtered and washed several times with water. The obtained crude product was purified by crystallization from hot ethanol (yield ~ 60–80%). The analytical data were confirmed by expected composition (Table 1). The ligands were also characterized by ^{1}H NMR and IR spectroscopy.

The synthesis of ligand is summarized in Fig. 1. However a detailed procedure is given in the following reactions:

The resulting ligands are:

- (4-Methoxyphenylazo)-5-sulfo-8-hydroxyquinoline (HL_1).
- (4-Methylphenylazo)-5-sulfo-8-hydroxyquinoline (HL_2).
- (4-Phenylazo)-5-sulfo-8-hydroxyquinoline (HL_3).
- (4-Chlorophenylazo)-5-sulfo-8-hydroxyquinoline (HL_4).
- (4-Nitrophenylazo)-5-sulfo-8-hydroxyquinoline (HL_5).

2.2. Synthesis of metal complexes

The appropriate ligand (0.01 mol) dissolved in ethanol (20 cm^3) was added dropwise into an ethanolic solution (20 cm^3) of metal salt (0.01 mol) with stirring. After the complete addition, 0.50 g of sodium acetate was added to the solution and the reaction mixture was refluxed for 2 h. The solution, thus obtained was concentrated to half of its original volume by evaporation using a hot plate and allowed to cool to room temperature. During this, a microcrystalline solid was separated, which was isolated by filtration, washed with hot water followed by ethanol and ether and dried in air.

2.3. Microbiological investigation

For this investigation the agar well diffusion method was applied (Alghool et al., 2010). The antibacterial activities of the investigated compounds were tested against two local Gram positive bacteria (*Bacillus cereus* and *Staphylococcus aureus*) and two local Gram negative bacteria (*Escherichia coli* and *Klebsiella pneumoniae*) on the nutrient agar medium. Also, it was tested against four local fungal species (*Aspergillus niger*,

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Table 2 Antibacterial activities of (4-alkylphenylazo)-5-sulfo-8-hydroxyquinoline and its metal complexes. Inhibition zone was recorded in mm.

Compound	Concentration μg/ml	Gram positive bacteria		Gram negative bacteria	
		Bacillus cereus	*Staphylococcus aureus*	*Escherichia coli*	*Klebsiella pneumoniae*
HL_1	50	−ve	−ve	5	3
	100	2	−ve	4	3
	150	2	1	4	4
CuL_1	50	−ve	−ve	−ve	4
	100	−ve	−ve	−ve	4
	150	7	−ve	−ve	3
NiL_1	50	1	1	1	−ve
	100	1	−ve	2	−ve
	150	1	1	2	−ve
HL_2	50	−ve	−ve	3	3
	100	−ve	−ve	4	−ve
	150	2	−ve	4	−ve
CuL_2	50	5	−ve	3	4
	100	−ve	−ve	3	3
	150	−ve	−ve	−ve	4
NiL_2	50	1	−ve	2	−ve
	100	−ve	−ve	−ve	−ve
	150	−ve	−ve	1	−ve
HL_3	50	2	−ve	2	2
	100	2.5	−ve	2	2
	150	3	1	2	4
CuL_3	50	2	1	4	4
	100	2	1	3	3
	150	2	1	3	3
NiL_3	50	−ve	1	1	−ve
	100	1	1	1	−ve
	150	1	1	1	−ve
HL_4	50	4	1	2.5	3
	100	5	−ve	2	4
	150	2	−ve	2	4
CuL_4	50	2.5	−ve	3	3
	100	3	−ve	3	3
	150	−ve	−ve	4	3
NiL_4	50	−ve	−ve	−ve	−ve
	100	1	−ve	3	−ve
	150	2	−ve	3	−ve
HL_5	50	−ve	1	3	3
	100	3	1	3	2
	150	4	−ve	3	3
CuL_5	50	3	−ve	4.5	3
	100	3	−ve	2	3
	150	4	−ve	2	4
NiL_5	50	−ve	−ve	2	−ve
	100	1	−ve	3	2
	150	2	−ve	2	−ve
Penicillin	50	1	2	1	−ve
	100	3	2	3	−ve
	150	3	2	3	−ve

Alternaria alternata, *Penicillium italicum* and *Fusarium oxysporium*) on the DOX agar medium. The concentrations of each solution were 50, 100 and 150 μg/ml. By using a sterile cork borer (10 mm diameter), wells were made in agar medium plates previously seeded with the test organism. 200 μl of each compound was applied to each well. The agar plates were kept at 4 °C for at least 30 min to allow the diffusion of the compound. The plates were then incubated at 37 °C or 30 °C for

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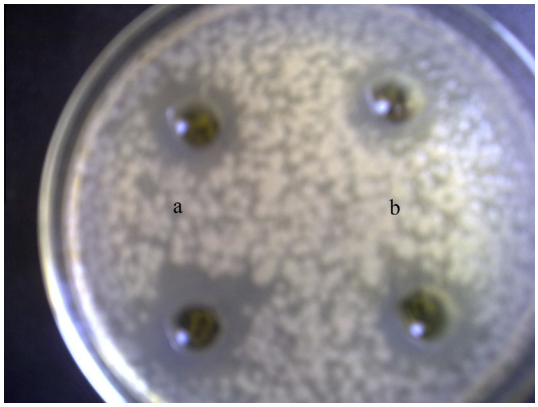

Figure 4 Effect of HL_2 and HL_5 on growth of *Klebsiella pneumoniae* on the nutrient agar medium using concentrations $a = 50$ μg/ml and $b = 150$ μg/ml.

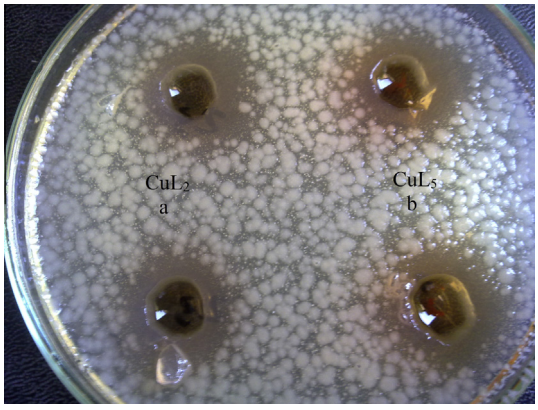

Figure 5 Effect of CuL_2 and CuL_5 on growth of *Klebsiella pneumoniae* on the nutrient agar medium using concentrations $a = 50$ μg/ml and $b = 150$ μg/ml.

bacteria and fungi respectively. Penicillin and miconazole were used as antibacterial and antifungal substrates respectively. The diameters of inhibition zone were determined after 24 h and 7 days for bacteria and fungi, respectively.

2.4. Measurements

Elemental microanalyses of the separated ligands and solid chelates for C, H, S, and N were performed in the Microanalytical Center, Cairo University, Egypt. The analyses were repeated twice to check the accuracy of the analyzed data. The ^{1}H-NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with DMSO-d_6 as the solvent and TMS as an internal reference. Infrared spectra were recorded as KBr pellets using a Pye Unicam SP 2000 spectrophotometer. Ultraviolet–Visible (UV–Vis) spectra of the compounds were recorded in nuzol solution using a Unicom SP 8800 spectrophotometer.

3. Results and discussion

3.1. Structure and stability

The presence of a sulfonate group in the quinoline ring confers special characteristics to the ligand, introducing changes in spectroscopic and structural properties of the metallic complexes.

It has been known that 8-hydroxyquinoline exists, in solution, in a monomer dimer equilibrium (El-Sonbati et al., 2002, 2010a, 2012b; Cook and Rotello, 2002; Albrecht et al., 1999). Our results of this paper suggest that in the monomeric form a strong intramolecular hydrogen bond is present. This is in agreement with previous results (Suzuki, 1967). The two such monomers lead to the dimer by forming an additional hydrogen bond yielding the bifurcated hydrogen bonds and H–N–H nitrogen bridges (Fig. 2A).

In addition to the two bifurcated intra/intermolecular OH...N hydrogen bonds (Figs. 1 and 3), two more intermolecular hydrogen bonding interactions are observed between nitrogen atom of the azo/azomethine group and hydrogen atom of the hydroxyl group. This additional H-bond does not influence the intramolecular distance which shows a band at a lower frequency than the intermolecular interaction. Reason for this behavior might be due to the additional H-bond which influences the hydrogen bonding ability of the sulfonyl group by electronic and/or steric factors. The overall structure of the dimer is close to planar with a slight shift of the two quinoline units from the plane. The two hydroxyquinoline units of the dimer (Fig. 2B′ and C_2) are in one plane. The intermolecular as well as intramolecular hydrogen bonding occur between the hydroxyl group and the quinoline nitrogen atom. The intermolecular hydrogen bond distance is shorter than the intramolecular one. This observation was also reported for other 8-hydroxyquinoline dimers and might be due to an unfavored small O–H–N angle for the intramolecular interaction (Jeffery et al., 1989; Cook and Rotello, 2002; Albrecht et al., 1999).

Hydrogen bonding represents one of the most versatile interactions that could be used for molecular recognition. In view of the large differences in the substituent effects (*e.g.*, the Hammett-type substituent constants for *p*-positions and sulfonyl group); it might be possible to tune the strength of the hydrogen bond effectively by linking the hydrogen-bonding site to a reaction center through a conjugated spacer, and by altering the charge state of the reaction center in the solution. At the hydrogen-bonding end, azo/azomethine is used as a proton acceptor to form a hydrogen bond with the OH group of ligand.

An electron-withdrawing bridge would be expected to increase the acidity of the proton donor and hence increase its binding ability. As the electron-withdrawing character of an azo group is relevant to the interesting signal-amplifying behavior (Suzuki, 1967) the results indicate that in the HL_n, the effects of the bridges are electron-withdrawing and electron-donating, respectively. Accordingly, the efficiency of sp^2-hybridized bridges is N═N > C═N.

Coggeshall and El-Sonbati et al. (Coggeshell, 1947; El-Sonbati et al., 2002a, 2004a, 2007, 2010a, 2012b) found three kinds of bonded –OH structures on the basis of the frequencies: (i) only oxygen is in the bridge while hydrogen is free, (ii) a polymer chain is formed in which both hydrogen and oxygen atoms participate in the hydrogen bond, and (iii) dimer associates are formed.

Intramolecular hydrogen bond between nitrogen atom of C═N(CN_{Py})/–N═N– (five/six-membered) system and hydrogen atom of phenolic hydroxyl hydrogen atom and hydrogen (C_8–OH) are illustrated in Fig. 2B, C and C′. Intermolecular

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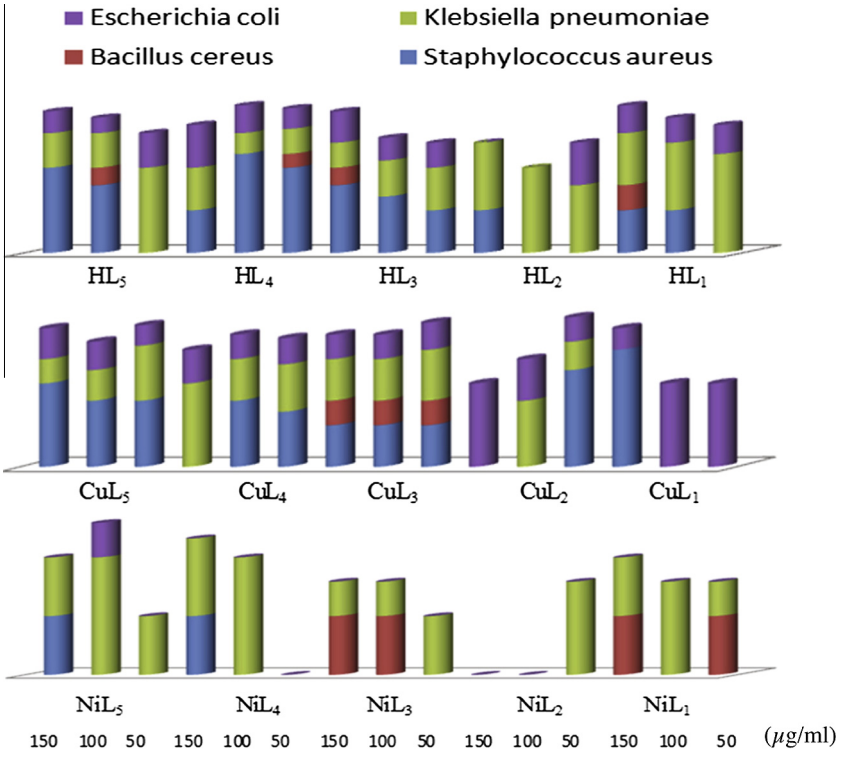

Figure 6 Antibacterial activity data of (4-alkylphenylazo)-5-sulfo-8-hydroxyquinolines (HL_n) and their metal complexes. Inhibition zones were recorded as mm.

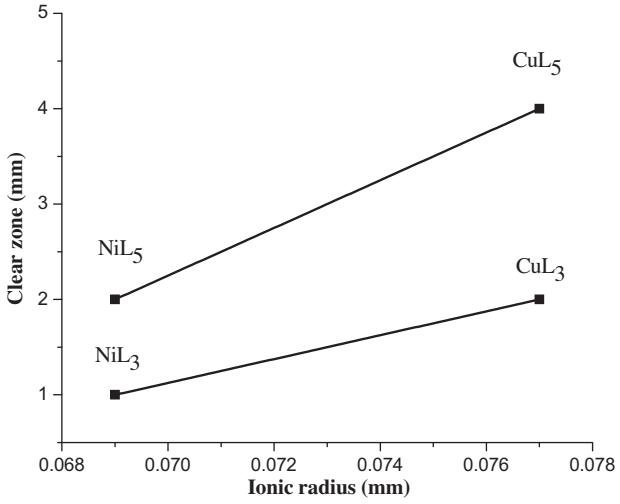

Figure 7 The relation between ionic radius and inhibition zone (mm) (In the case of using concentration = 150 μg/ml against *Bacillu scereus*).

hydrogen bonding can form a cyclic dimer through the O–H—OH type between C_8–OH/═N of one molecule and C_8–OH/N═N group of another one (Fig. 3H, G and F) and/or ----N type between C_8–OH of one molecule and CNpy/–N═N– of another (Fig. 3D).

In general, hydrogen bonds involving OH groups are proton donors and their O atoms are proton acceptors. Both intra and intermolecular OH–N may form a number of structures in a simultaneous equilibrium.

3.2. ^1H NMR spectra

The ^1H NMR spectra of all the ligands were recorded in DMSO-d_6 at room temperature. The signal due to methyl and methoxy proton appeared as a singlet at 1.55 and 3.84 ppm, respectively. In the aromatic region, a few doublets and in few cases some overlapping doublets/multiplets are observed in the range δ 6.78–8.40 ppm. These doublets/multiplets are due to aryl protons of three benzene rings. Another singlet corresponding to one proton for all compounds is observed in the range $\delta \sim 9.2$–10.40 ppm. This signal disappeared when a D_2O exchange experiment was carried out. It can be assigned either to OH or NH, in either case it is strongly deshielded because of hydrogen bonding with the other atom (N/O) (Figs. 2 and 3). It may be noted that the integration of this signal perfectly matches with one proton and there is no other fragment(s) of this signal, which suggest that only one tautomeric form of the ligand exists in the solution under the experimental conditions. Comparing with the solid state study, we prefer to assign this signal to OH, however, assignment of this peak to NH cannot be ruled out provided solid state structural evidence is not considered (Jadeja et al., 2004). As reported in previous studies (El-Sonbati et al., 2011; Shoair et al., 2001), this hydrogen bonding lead to a large deshielding of these protons. The shifts are in the sequence: p-NO_2 > p-Cl > H > p-OCH_3 > p-CH_3. The appearance of signals due to HC═N [~8.94 ppm (1H)] protons of the same positions in the ligand and its diamagnetic complexes shows the non-involvement of this group in coordination (Shoair et al., 2001).

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Table 3 Antifungal activities of (4-alkylphenylazo)-5-sulfo-8-hydroxyquinoline and its metal complexes. Inhibition zone were recorded as mm.

Compound	Concentration μg/ml	*Fusarium oxysporium*	*Penicillium italicum*	*Aspergillus niger*	*Alternaria alternata*
HL_1	50	1	−ve	−ve	−ve
	100	1.5	−ve	4	−ve
	150	1.5	−ve	1	−ve
CuL_1	50	1	−ve	−ve	−ve
	100	−ve	−ve	−ve	−ve
	150	−ve	−ve	−ve	−ve
NiL_1	50	−ve	−ve	−ve	−ve
	100	1	−ve	−ve	1
	150	1	−ve	−ve	2
HL_2	50	−ve	−ve	−ve	−ve
	100	1.5	−ve	−ve	−ve
	150	1	−ve	−ve	−ve
CuL_2	50	1.5	−ve	−ve	−ve
	100	−ve	−ve	−ve	−ve
	150	1	−ve	−ve	−ve
NiL_2	50	−ve	−ve	−ve	−ve
	100	−ve	−ve	−ve	−ve
	150	−ve	−ve	−ve	−ve
HL_3	50	2	−ve	−ve	−ve
	100	2	−ve	−ve	−ve
	150	2	−ve	−ve	−ve
CuL_3	50	2	−ve	−ve	−ve
	100	1	−ve	−ve	−ve
	150	1	−ve	−ve	−ve
NiL_3	50	−ve	−ve	−ve	−ve
	100	−ve	−ve	−ve	−ve
	150	−ve	−ve	−ve	−ve
HL_4	50	−ve	−ve	−ve	−ve
	100	−ve	−ve	−ve	−ve
	150	1.5	−ve	−ve	1
CuL_4	50	−ve	−ve	−ve	−ve
	100	1	−ve	−ve	−ve
	150	2	−ve	−ve	−ve
NiL_4	50	1.5	−ve	−ve	−ve
	100	−ve	−ve	−ve	−ve
	150	−ve	−ve	−ve	−ve
HL_5	50	1	−ve	−ve	2
	100	1	−ve	−ve	3
	150	2	−ve	−ve	1
CuL_5	50	1.5	−ve	−ve	−ve
	100	−ve	−ve	−ve	−ve
	150	−ve	−ve	−ve	−ve
NiL_5	50	−ve	−ve	−ve	−ve
	100	−ve	−ve	3	−ve
	150	−ve	−ve	−ve	−ve
Miconazole	50	2	1	1	5
	100	3	1	3	6
	150	3	2	4	6

3.3. Electronic spectra

HL_n exhibited bands at 32,500–32,150 cm^{-1} (CN) (π–π^*), 33,450–33,340 cm^{-1} (H-bonding and association), 40,038–39,460 cm^{-1} (phenyl) (Ph–Ph*, π–π^*) and 29,340–29,230 cm^{-1} transition of phenyl rings overlapped by a composite broad (π–π^*) of the azo structure. The band due to the $n \rightarrow \pi^*$ transition obtained in the visible region is

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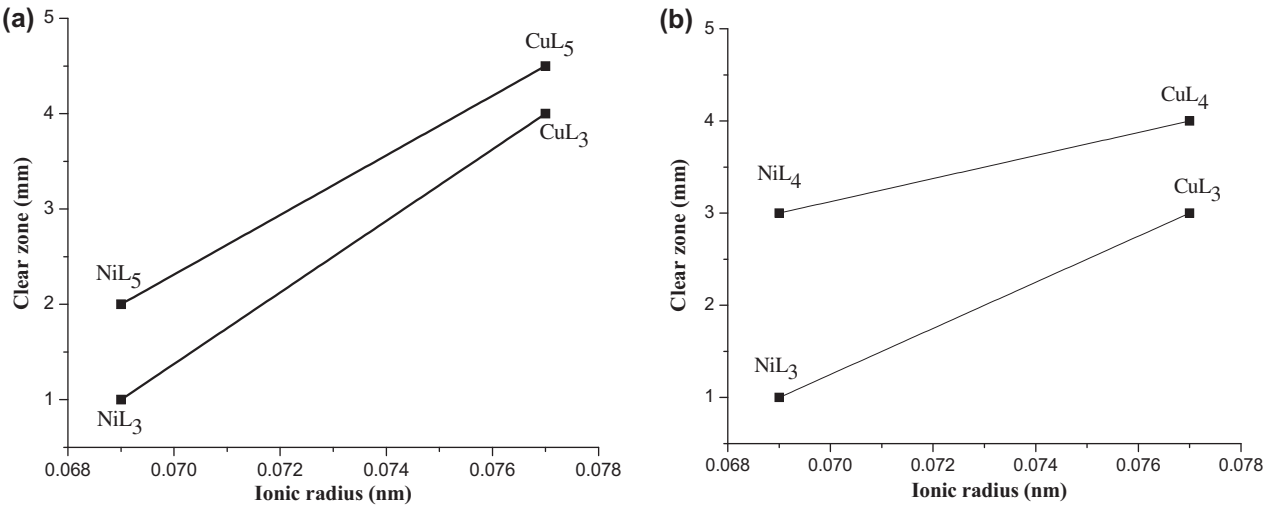

Figure 8 The relation between ionic radius and inhibition zone (mm) (In the case of using concentrations $a = 50$ μg/ml and $b = 150$ μg/ml against *Escherichia coli*).

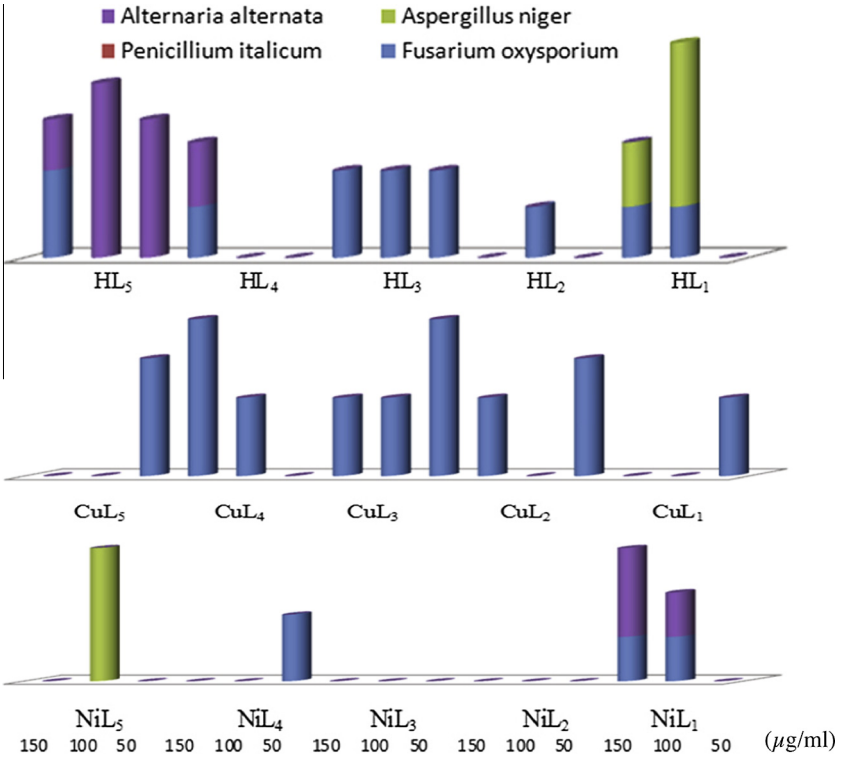

Figure 9 Antifungal activity data of (4-alkylphenylazo)-5-sulfo-8-hydroxyquinolines (HL_n) and their metal complexes. Inhibition zones were recorded as mm.

associated mainly with the color of the respective compound (El-Sonbati et al., 2012b). The band due to $\pi \rightarrow \pi^*$ transition moves to lower energy. These shifts or the disappearance of the bands is indicative of coordination of the ligands to M(II). The position of their bands varied from one dye to the other which may be attributed to the *p*-phenylazo substituent's variable donating power.

In general, most of the azo compounds give spectral localized bands in the wavelength range 46,620–34,480 cm^{-1} and 31,250–270, 370 cm^{-1}. The first region is due to the absorption of the aromatic ring compared to ^1B_b and ^1L_b of mono substituted benzene and the second region is due to the conjugation between the azo group and the aromatic nuclei with intermolecular charge transfer resulting from π-electron migration to the diazo group from electron donating substituents. The *p*-substituents increase the conjugation with a shift to a longer wavelength. Most of the simple *p*-substituted compounds are in the azoid form in cyclohexane and alcohols. The substituted

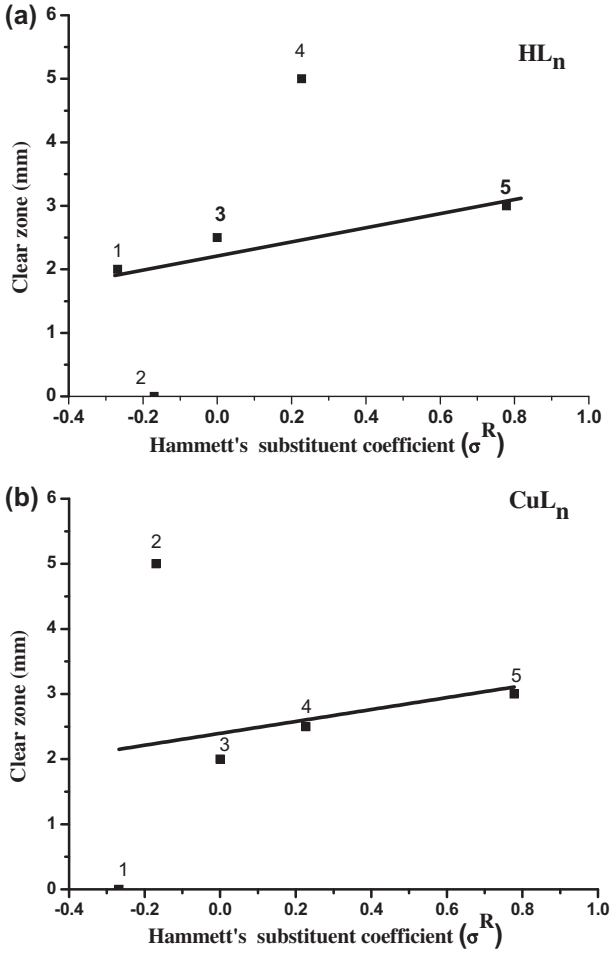

Figure 10 The relation between Hammett's substitution coefficient (σ^R) and inhibition zone (mm) (In the case of using concentrations a = 100 μg/ml (HL_n) and b = 50 μg/ml (CuL_n) against *Bacillus cereus*).

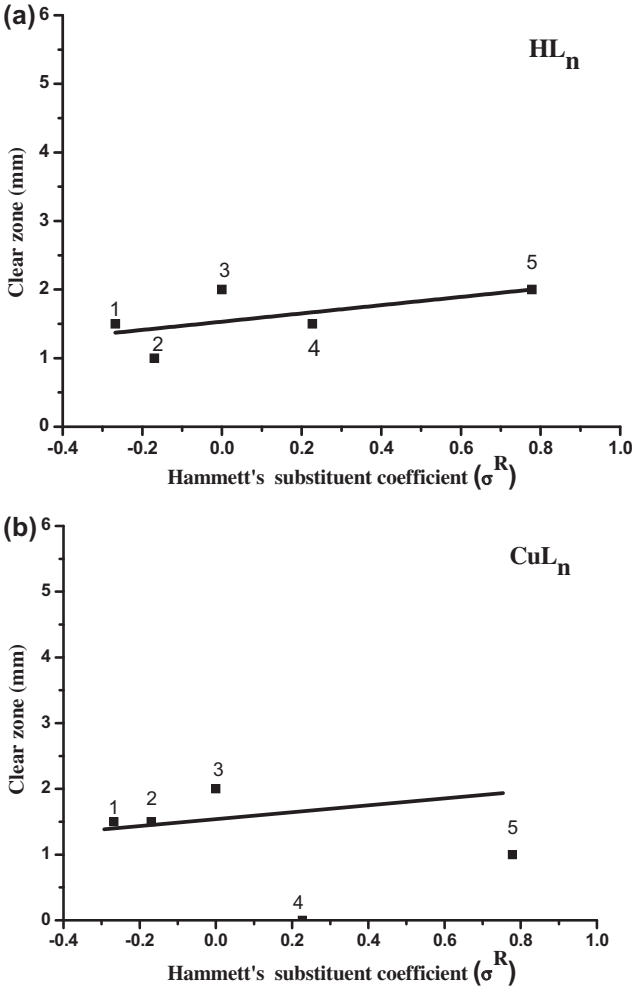

Figure 11 The relation between Hammett's substitution coefficient (σ^R) and inhibition zone (mm) (In the case of using concentrations a = 150 μg/ml (HL_n) and b = 100 μg/ml (CuL_n) against *Fusarium oxysporium*).

effect is related to the Hammett's constant values (El-Sonbati et al., 2010c, 2012b). The position of the π–π^* transition of the azo groups remains one of the most interesting unanswerable questions of molecular spectroscopy. For azo benzenes, as the possibilities of the mesomerism became greater, the stabilization of the excited state is increased relative to that of the ground state and a bathochromic shift of the absorption bands follows (El-Sonbati et al., 2010c). Based on the MO theory the energy terms of the molecular orbital became more closely spaced as the size of the conjugated system increases (Jean, 2004). Therefore, with every additional conjugated double bond the energy difference between the highest occupied and the lowest vacant π-electron level became smaller and the wavelength of the first absorption band corresponding to this transition is increased. The azo group can act as a proton acceptor in hydrogen bonds (El-Sonbati et al., 2010c, 2012b). The role of hydrogen bonding in azo aggregation has been accepted for some time.

3.4. Microbiological investigation

The antimicrobial activity of HL_n ligand was tested against bacteria and fungi; we used more than one test organism to increase the chance of detecting their antimicrobial activities. The used organisms in the present investigations included two Gram positive bacteria (*B. cereus* and *S. aureus*) and two Gram negative bacteria (*E. coli* and *K. pneumoniae*) in addition to four species of fungi (i.e. *A. niger*, *P. italicum*, *Alternaria alternata* and *F. oxysporium*). The results of the antibacterial activities of the synthesized compounds are recorded in Table 2. All the used HL_n and some of their metal complexes were found to have antibacterial activity against Gram negative bacteria namely; *E. coli* (inhibition zone of HL_1 = 5 and 4 mm at concentration = 50 and 100 μg/ml) and inhibition zone of HL_4 = 2 mm and CuL_4 = 3 mm and $NiCl_2$ = 3 mm at concentration = 100 μg/ml). In addition to that *K. pneumoniae* was also affected by HL_n and their metal complexes i.e. (inhibition zone of HL_1 = 3 mm and CuL_1 = 4 mm at concentration = 50 μg/ml) and (inhibition zone of HL_3 = 2 mm and CuL_3 = 4 mm at concentration = 50 μg/ml. CuL_2, CuL_3 and CuL_5 were found to have high antibacterial activity than HL_2, HL_3 and HL_5 against *K. pneumoniae*, this means CuL_n complexes are more active

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than HL_n as shown in Figs. 4 and 5. Whereas the HL_n and their derivatives also have effect against Gram positive bacteria; namely *B. cereus* (inhibition zone of HL_3 = 2 mm and HL_4 = 4 mm at concentration = 50 μg/ml) and inhibition zone of CuL_3, CuL_4 and CuL_5 = 2, 2.5 and 3 mm, respectively at concentration = 50 μg/ml). But very low effects were recorded against *S. aureus*. HL_4, HL_5 and HL_1 are more active than penicillin against *B. cereus*, *E. coli* and *K. pneumoniae* as shown in Fig. 6.

Zhandarev et al. (2006) found that dichlorotetrahydroquinolinol and dichloromethyloxyquinolinol caused the maximum antibacterial effect with respect to Gram negative bacterial species (i.e. *E. coli*). The same previous authors recorded that some quinolinols and their tetrahydro derivatives caused pronounced growth inhibition of *S. aureus*. The results (Table 2) reveal that the ligand is moderately toxic against bacteria, while all the chelates are more toxic than ligand. Among all the chelates the Cu^{2+} chelates are toxic against bacteria, also Cu^{2+} complexes are more active than Ni^{2+} complexes against *B. cereus*, *E. coli* and *K. pneumoniae*. The relation between the values of inhibition zone and ionic radius for complexes is shown in Figs. 7 and 8 and it is clear that the values of inhibition zone increase with increasing ionic radius. Our results of the antifungal activities of the synthesized compounds are recorded in Table 3. The results of the examination of antifungal activity of HL_n ligands (Table 3) revealed that the ligands have low toxicity than their complexes against fungi as shown in Fig. 9. Patel (2009) found that 5-(4-N,N-Diethylaminosulfonly phenylazo)-8-hydroxy quinolines and their metal chelates have moderate and high toxicity against some fungi including *A. niger* and *Penicillium expansum*. The same previous author found that Cu^{2+} chelates are more toxic against the tested fungi than other chelates.

As shown in Tables 2 and 3, the values of inhibition zone for ligands (HL_n) are related to the nature of the *p*-substituent as they increase according to the following order *p*-(NO_2 > Cl > H > CH_3 > OCH_3) (El-Sonbati et al., 2011, 2012a; El-Ghamaz et al., 2011, 2012; Abou-Dobara et al., 2013). This can be attributed to the fact that the effective charge experienced by the d-electrons increased due to the electron withdrawing *p*-substituent (HL_4 and HL_5) while it decreased by the electron donating character of HL_1 and HL_2. This is in accordance with that expected from Hammett's constant σ^R as shown in Figs. 10 and 11 correlates the values of inhibition zone (mm) with σ^R, it is clear that these values increase with increasing σ^R. It is important to note that the existence of a methyl and/or methoxy group enhances the electron density on the coordination sites and simultaneously decreases the values of inhibition zone.

4. Conclusion

The results arising from the present investigations confirm that the hydroxyquinoline exists, in solution, in a monomer dimer equilibrium. The results suggest that in the monomeric form a strong intramolecular hydrogen bond is present. Two monomers lead to the dimer by formation of an additional hydrogen bond yielding the bifurcated hydrogen bonds and H–N–H nitrogen bridges (Fig. 2A). The dimer is able to dissociate, while the intramolecular interaction can be broken if appropriate hydrogen bond acceptors are attached which act as competitors to the quinoline nitrogen atoms as was observed (Fig. 2B′). In conclusion, the results of the present study indicate that the selected (4-alkylphenylazo)-5-sulfo-8-hydroxyquinoline (HL_n) ligands are suitable for building a supramolecular structure. Moreover, the azo and/or hydrazo compounds experience photochemical isomerization and are, therefore, of interest for applicative purposes. The antimicrobial activity was tested against *B. cereus, S. aureus*, *E. coli*, *K. pneumoniae*, *A. niger*, *Alternaria alternata*, *P. italicum* and *F. oxysporium* and the results proved that HL_3, $CuCl_3$, HL_5 and $CuCl_5$ have antibacterial activity against *E. coli*, *K. pneumoniae* and *B. cereus*.

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